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ONE-PHONON RAMAN SCATTERING FROM ARRAYS OF SEMICONDUCTOR
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We re-consider Raman scattering by LO-type phonons in a small semiconductor crystal and derive a simple formula taking into account the higher order confined phonon modes, to describe the asymmetric Raman lineshapes observed experimentally. For a single crystalline sphere, we explicitly calculate the relative contributions of the confined modes with different values of the radial quantum number. For arrays of such spheres, we argue that, apart from a superposition of the above contributions from individual scatterers, there exists a collective scattering by a coherent mode which involves many spheres, unless their concentration is too small. This collective scattering is determined by an effective dielectric function of the composite medium and peaks near the Fröhlich frequency. We apply these principles to the analysis and modelling of Raman spectra taken from CdS doped SiO₂ films. © 1997 Published by Elsevier Science Ltd

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1. INTRODUCTION

The effects of reduced space dimensions on the optical properties of semiconductor nano-crystals are the subject of much current interest [1]. Phonons in these materials are interesting from two points of view [2]. First, the electron-phonon interaction plays a critical rôle in the optical properties. Secondly, it may be possible, through Raman measurements, to determine the size of the nano-crystals. However, the crystal size effects on the Raman spectra and on the electron-phonon interaction are still somewhat controversial [3]. In most cases, the first-order Raman line redshifts and broadens with asymmetry towards the low-frequency side as the nano-crystal size decreases [2–5]. Unexpected upward shifts have also been observed and attributed to compressive strains due to the glass matrix [6], or to impurities in the nano-crystals [7].

According to the classical work of Ruppin and Englman [8], in small ionic crystals there exist bulk-like optical modes, the so called Fröhlich mode corresponding to a uniform polarization of the nano-crystal, and also surface optical modes. The Fröhlich mode is only IR-active [9] while the surface modes usually contribute much more weakly than internal modes to Raman scattering [5] despite the fact that for the small nano-crystals a significant part of the atoms are surface atoms. To describe the scattering by the internal modes, a simple phenomenological model was proposed some ten years ago [10], which has been used by most experimentalists studying Raman spectra from various semiconductor nano-crystal systems [4, 11, 12]. In fact, the model and the widely used formula were proposed much earlier [13] for Raman scattering by disordered materials. The central part of the model is the phonon weighting function. There is arbitrariness in the choice of this function, since it has no clear physical meaning in the case of small crystals (in contrast to the case of disordered materials where it is the displacement-displacement correlation

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function). It is *not* an eigenfunction of the dynamical equation of motion because the expression [10] for the Raman intensity involves an integration over bulk phonon wavevectors instead of summation over the appropriate quantized eigenmodes. Accordingly, this model cannot reliably give a satisfactory description of the Raman spectra [14] unless one constructs a sophisticated weighting function with enough degrees of freedom.

The scope of the present paper is to propose a formula, as simple as that of ref. [10], describing the one-phonon Raman scattering by nano-crystals and, unlike that in ref. [10], taking properly into account the changes in the spectrum of phonons due to their spatial confinement. Also, we discuss a collective Raman scattering by small (of the order of the light wavelength in size) regions of the composite medium which contain a sufficient number of nano-crystals.

2. SCATTERING FROM A SINGLE SMALL CRYSTAL

We start with a known expression for the one-phonon cross-section (Stokes component) [15, 16]:

$$\frac{d^2\sigma}{d\Omega d\omega_S} = \left(\frac{\eta_I}{\eta_S}\right) \frac{\hbar\omega_I\omega_S^3}{\pi c^4} (n(\omega) + 1) \times \sum_{r, \kappa, \alpha} e^{-i(k_I - k_S)R_{r\kappa}} a_\alpha(\kappa) a_{\alpha'}(\kappa') e^{i(k_I - k_S)R_{r\kappa}} \times \text{Im } G_{\alpha\alpha'}(r', \kappa', r, \kappa; \omega) \quad (1)$$

where

$$a_\alpha(\kappa) = \sum_{\beta, \gamma} e_S^\beta e_I^\gamma P_{\beta\gamma}^\alpha(\kappa),$$

$$P_{\beta\gamma}^\alpha(\kappa) = \frac{\partial \chi_{\beta\gamma}}{\partial u_\alpha}$$

$\chi_{\beta\gamma}$ is the polarisability tensor, u_α are the displacement components, η_I , k_I and e_I , and η_S , k_S and e_S are the refraction coefficient, wavevector and polarization vector for the incident and scattered waves, respectively, r and r' run over unit cells, κ and κ' denote different atoms within one unit cell, α, β, γ stand for Cartesian coordinates, G is the one-phonon Green function defined as follows:

$$G_{\alpha\beta}(r', \kappa', r, \kappa; \omega) = \sum_{\nu} \frac{u_{\nu, \alpha}(r, \kappa) u_{\nu, \beta}(r', \kappa')}{\omega^2 - \omega_\nu^2} \quad (2)$$

where ν enumerates the phonon eigenstates.

For large crystals, $\nu \Rightarrow (q; j)$, q and j being the phonon wavevector and branch number, respectively,

$$u_{qj}(r, \kappa) \sim e^{iqR_{r\kappa}},$$

the summations over r, r' give $V\delta(k_I - k_S - q)$ (V is the scattering volume), and one arrives at a known expression for the Raman cross-section, containing the spectral density of optical phonon states with $q = 0$. For a crystal without disorder, the latter is just a δ -function at the appropriate frequency.

For a small crystal, two facts must be taken into consideration:

(i) the phonon spectrum is now described by a different set of quantum numbers;

(ii) even if phonons still can be approximately described by the wavevector, the integration over just a small volume leads to broadening of the δ -function expressing the quasi-momentum conservation.

To explore these ideas, let us consider a small crystal of a simple (e.g. spherical) shape made of an ionic binary compound. Then

$$P_{\alpha\beta}^\gamma(\kappa) = (-1)^\kappa \hat{p}_{\alpha\beta, \gamma} \quad (3)$$

$$u_\nu(r, \kappa) = \frac{(-1)^\kappa}{\sqrt{M_\kappa}} e_\nu(r) \left(\frac{\mu}{M_\kappa}\right)^{1/2} \Psi_\nu(r) \quad (4)$$

for optical phonons, where e_ν is the phonon polarization vector, M_κ are atomic masses, μ is the reduced atomic mass, \hat{p} is a constant tensor and $\Psi_\nu(r)$ is an envelope function. Using (2)–(4), (1) reduces to

$$\frac{d^2\sigma}{d\Omega d\omega_S} \sim (n(\omega) + 1) \text{Im} \frac{1}{\mu} \sum_{\nu} \frac{|\varphi_\nu|^2}{\omega^2 - \omega_\nu^2 - i0} \quad (5)$$

where

$$\varphi_\nu = \sum_r A_\nu(r) \Psi_\nu(r) e^{i(k_I - k_S)R_r} \approx \frac{1}{V} \int A_\nu \Psi_\nu dR \quad (6)$$

is an overlap integral, R_r being the radius vector of the r -th unit cell (of volume v), and

$$A_\nu(R) = \sum_{\alpha, \beta, \gamma} \hat{p}_{\alpha\beta, \gamma} e_I^\alpha e_S^\beta e_\nu^\gamma(R)$$

depends on the phonon symmetry and scattering geometry.

Phonons in small spherical crystals were considered in [9, 17]. There are just two types of Raman-active modes with $l = 0$ and 2 (l is the orbital quantum number), i.e. A_ν is non-zero for only these modes. The most important contribution to the one-phonon Raman scattering corresponds to $l = 0$. This mode is excited for parallel polarizations of the incident and scattered light. According to [9],

$$\Psi_n(R) = C j_l(\zeta_n \frac{R}{R_0}); \quad n = 1, 2, \dots \quad (7)$$

where R_0 is the sphere's radius, j_l is the Bessel spherical function, C is a normalisation constant and ζ_n is

the n -th root of j_1 . The corresponding vibrational frequencies are:

$$\omega_n^2 = \omega_{LO}^2 - \beta_{LO}^2 \left(\frac{\zeta_n}{R}\right)^2 \quad (8)$$

with ω_{LO} and β_{LO} being the bulk LO frequency and the LO dispersion curve bending parameter, respectively. The polarization of these confined modes e_R is, of course, independent of n and, since

$$\hat{p}_{\alpha\beta,\gamma} \sim \delta_{\alpha\beta} e_R^\gamma$$

the A factor can be removed from (6) and (5).

Using (5)–(7), we obtain

$$\frac{d^2\sigma}{d\Omega d\omega_S} \sim (n(\omega) + 1) \operatorname{Im} \sum_n \frac{B_n}{\omega^2 - \omega_n^2 - i0} \quad (9)$$

where

$$B_n = 8\pi R_0^3 \left[\frac{2(1 - \cos \zeta_n) - \zeta_n \sin \zeta_n}{3\zeta_n \cos \zeta_n - (3 - \zeta_n^2) \sin \zeta_n} \right]^2 \quad (10)$$

3. SCATTERING FROM AN ENSEMBLE OF SMALL CRYSTALS

Since the vibrational mode considered above does not produce any electric field outside the sphere, there is no interaction associated with this mode between the nano-crystals. Also, due to distribution of their sizes, we can rule out any coherence of scattering by different spheres. Therefore, the Raman cross-section of an array of scatterers is simply a superposition of their individual contributions. The latter is determined by formulae (8)–(10). The array cross-section is, roughly speaking, proportional to the volume fraction f of semiconductor. The array scattering is also supposed to be fully polarized if the composite medium is isotropic on the average.

If an "interaction volume" of the light includes many nano-crystals, there should be another contribution to Raman scattering due to a collective vibrational–electromagnetic excitation of the Fröhlich type. For a single sphere, the Fröhlich mode is Raman-inactive [9]. However, a piece of the composite medium containing many spheres is described by an effective dielectric function ϵ^* whose zeros correspond to longitudinal-type collective excitations which involve mechanical displacements within the spheres and which are purely electromagnetic in between. An electromagnetic wave interacting coherently with this piece of the medium would "see" these excitations. Therefore we should expect for this kind of scattering in the backscattering geometry [15]

$$\frac{d^2\sigma}{d\Omega d\omega_S} \sim (n(\omega) + 1) \operatorname{Im} \left(-\frac{1}{\epsilon^*}\right) N_c \quad (11)$$

where N_c is the number of the "collective scatterers".

The effective dielectric function of a composite containing separate (spherical) inclusions embedded in a dielectric matrix can be calculated using an approach based on the classical Maxwell-Garnett (MG) theory [18] but using a renormalised polarizability of the inclusions which can be related to the usual one by a kind of the Dyson equation. This (RMG) approach allows for taking into account a continuous distribution of sizes of the spheres if their dielectric function $\epsilon_s(R_0)$ is known [19]. Since the Fröhlich frequency should be much less dependent on R_0 than the confined LO phonon frequency, the dielectric function of the spheres can be taken as for bulk, i.e.

$$\epsilon_s = \epsilon_\infty \left(1 + \frac{\omega_{TO}^2(\epsilon_0 - \epsilon_\infty)}{\omega_{TO}^2 - \omega^2 - i\omega\Gamma_{TO}}\right) \quad (12)$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, ω_{TO} is the bulk phonon frequency and Γ_{TO} is TO phonon damping. As $f \rightarrow 0$, the effective LO frequency (corresponding to the peak of $\operatorname{Im}(-\epsilon^*)^{-1}$) tends, of course, to the Fröhlich frequency ω_F but for finite f it lies above ω_F and below ω_{LO} [19].

For higher filling fractions ($f \geq 0.3$), probably more relevant is a self-consistent mean-field approximation known as the Bruggeman model (BM) [20]. This approach is widely used to describe various properties of composite media.

The interaction volume which should be taken as the size of the collective scatterer is of the order of $\lambda^2 \xi_c$, where λ is the light wavelength and $\xi_c \sim f^{-1}$ is its coherence length. Therefore the number of the collective scatterers $N_c \sim f$ and, since approximately $\operatorname{Im}(-\epsilon^*)^{-1} \sim f$, the Raman cross section is proportional to f^2 for this mechanism, implying the condition of the collective scattering $f \gg R_0^3/(\lambda^2 \xi_c)$ satisfied. The different collective scatterers can be considered as independent and randomly oriented cylinders, because, apart from the Raman scattering, there is also elastic scattering of light, and the partial waves propagate in all possible directions (which define the collective scatterer's orientations) within the medium. Consequently, the inelastically scattered light should be least polarized in this case [15].

4. RESULTS AND DISCUSSION

Formulae (8)–(10) have been applied to describe Raman spectra of CdS nano-crystals of the size range of 4–10 nm embedded in SiO₂ glass films grown by the magnetron RF-sputtering technique with post-deposition annealing. Details of sputtering and an-

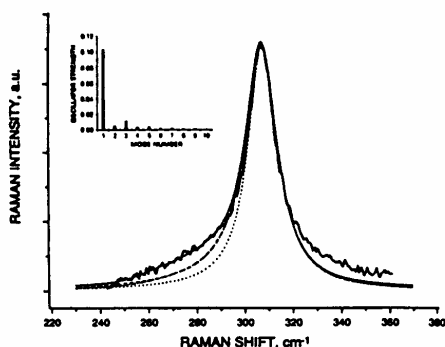


Fig. 1. Experimental (bold curve) and theoretical Raman spectra of a rf-sputtering grown CdS/SiO₂ film. The theoretical curves are as follows: dashed line - confined LO modes with $n = 1, \dots, 10$ assuming a Gaussian distribution of sphere's sizes; dashed-dotted line - spheres of one size only are considered; dotted line - single Lorentzian for the principal mode in the sphere of $R_0 = 50\text{\AA}$; full fine curve is the sum of the contribution of the LO modes (dashed line) and that of the collective mode (see also Fig. 2). The insert shows the relative contributions of the modes with different n calculated according to equation (10).

nealing regimes have been reported before [21]. X-ray studies showed zinc-blende structure of the nano-crystals. One of these spectra taken at room temperature in the backscattering geometry using an Ar laser and a Jobin Yvon T64000 spectrometer (resolution better than 1 cm^{-1}) is shown in Fig. 1. The theoretical spectrum (the dashed line) fits the central part of the experimental peak very well using just two adjustable parameters: the mean radius of the spheres ($R_0 = 50\text{\AA}$ in this case) and the natural Lorentzian linewidth ($\Gamma_{LO} = 12\text{ cm}^{-1}$). It reproduces the asymmetry due to the contribution of the modes with $n \geq 2$ (for comparison, a Lorentzian centered at the first confined LO mode is also shown in Fig. 1). As can be seen from the insert, the odd modes contribute more strongly than the even ones.

Since the bulk LO phonon dispersion curve of CdS is relatively flat (β_{LO} is rather small), the Raman lineshape is rather insensitive to the distribution of sphere's sizes. The curves of Fig. 1 calculated first for spheres of one size and then for the spheres with a Gaussian distribution of the radii almost coincide.

At the same time, the experimental spectral peak possesses a very broad pedestal which implies a wide band of Raman-active phonon states not included in the model. As is known [22], neither confinement nor disorder in nano-crystals can produce phonon states above the upper limiting frequency of the bulk ma-

terial (307 cm^{-1} for CdS) unless the effects of a new chemical binding or compressive stress are involved. In our case, since the peak is always below 307 cm^{-1} , the most natural explanation of the high-frequency tail may be as follows. The CdS films were grown on substrates of a common glass possibly containing ZnO. During the heat treatment Zn could diffuse into the film leading to the formation of some Cd_{1-x}Zn_xS nano-crystals [7], with x decreasing as the distance from the interface increases. Cd_{1-x}Zn_xS is an one-mode alloy displaying an LO frequency increasing with x almost linearly [16], so some of the spheres situated closer to the interface can produce LO-type vibrations of frequency higher than 307 cm^{-1} .

A low-frequency tail is often observed for nano-crystal semiconductor systems [2, 4]. It is tempting to attribute it to the collective scattering described in the previous section. The lineshape for this kind of scattering was calculated according to (11) using both the RMG and BM approximations. The results thus obtained for $f = 0.07$ are shown in Fig. 2. The two models give rather different lineshapes. If the difference in the dielectric functions of the spheres and the matrix is large (as is the case here), the use of the BM approximation is not justified for very small f (see discussion in [19]). Nevertheless, it is often applied, with some success, to composite systems with small volume fractions of inclusions (e.g. [23]). Surprisingly, the collective scattering lineshape calculated this way fits very well the difference between the experimental and theoretical spectra of Fig. 1 which is plotted in Fig. 2. This can also be seen from Fig. 1 where the full curve represents a superposition of the two lineshapes. Of course, this fact does not yet prove the assignment of the low-frequency tail to the collective Raman scattering mode. A possible contribution of the surface optical (SO) mode of a single sphere with $l = 2$, whose frequency, according to the formula given by [8], is about 279 cm^{-1} for the system studied here, cannot be disregarded. In fact, this is a common explanation of the low-frequency part of the Raman lineshape [4, 5]. The only paper of which we are aware claiming the observation of the Fröhlich mode (that is, of the collective mode) in Raman spectra is ref. [3]. It seems to be rather difficult to distinguish the contributions coming from the SO modes and the collective longitudinal mode, because both of them are expected to be depolarized [15, 17] and it is practically impossible to calculate and compare the absolute values of the scattering cross-sections. A study of the dependence of the low-frequency tail on the volume fraction of semiconductor could possibly distinguish collective scattering from that due to the SO modes, since it should be dif-

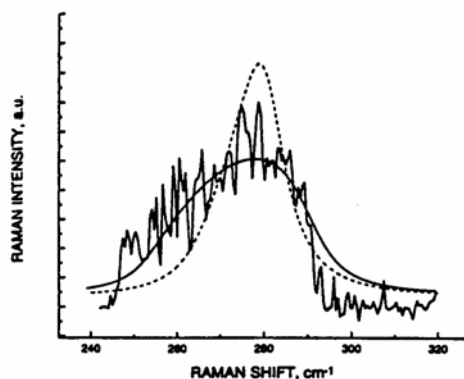


Fig. 2. Raman lineshapes for the collective scattering mechanism calculated using the BM (full curve) and RMG (dashed curve) models. In both cases $\Gamma_{LO} = 15 \text{ cm}^{-1}$, $f = 0.07$. Also shown (bold curve) is the difference between the experimental spectrum and the overall LO lineshape of Fig. 1. The ordinate scale is multiplied by a factor of 10 compared to Fig. 1.

ferent for the discussed modes.

We do not have such a set of well characterized similar samples of different f . In addition to rf-sputtering grown samples, we have also studied a CdS/SiO₂ film grown by the sol-gel technique [24], with the estimated filling fraction $f \approx 0.1$. Its Raman spectrum shown in Fig. 3 was fitted in the same way as that of Fig. 1. Again, the central part of the peak is well reproduced by the confined mode model (note that the mean radius $\bar{R}_0 = 21 \text{ \AA}$ is much smaller for this sample, which results in the position of its maximum shifted down to 301 cm^{-1} , compared to 306 cm^{-1} for the rf-sputtering grown sample). However, to reproduce its low-frequency (below 285 cm^{-1}) part, we had to take a higher value of the relative weight of the collective scattering than for the spectrum of Fig. 1, in qualitative agreement with the conclusion of Sec.3 that this effect should be proportional to f^2 . Furthermore, changing the exciting wavelength for 514.5 nm (that is, going further off resonance and making the condition for the collective scattering be more likely satisfied), the relative contribution of the additional mode is enhanced, as can be seen from the insert of Fig. 3. Lastly, this additional excitation can hardly be identified as the individual sphere's surface mode, since it lies well below the SO frequency in this case. On the contrary to the SO mode, the position of the $\text{Im}(-\epsilon^*)^{-1}$ peak depends on f . Thus, it seems much more plausible that the low-frequency tail of the lLO peak in our non-resonant Raman spectra is due to the collective mode and not the SO one.

In summary, we proposed a simple formula (9) for

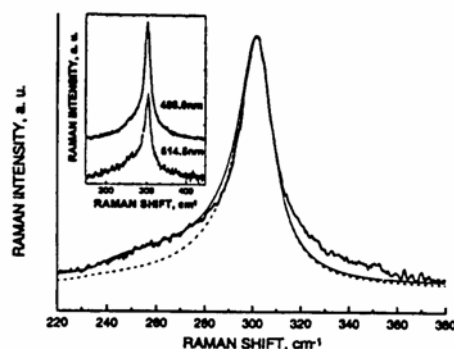


Fig. 3. Experimental (bold curve) Raman spectrum of a sol-gel grown CdS/SiO₂ film obtained with $\lambda_{exc} = 488 \text{ nm}$ and its theoretical fit (fine full curve), which is a sum of the contributions of the collective and confined modes. Dashed curve includes only the confined modes calculated assuming $\Gamma_{LO} = 15 \text{ cm}^{-1}$, $\bar{R}_0 = 21 \text{ \AA}$ and Gaussian distribution of the sphere's radii with a standard deviation of 5 \AA . The insert shows the effect of the exciting wavelength.

the Raman cross-section of perfectly confined LO-type modes with $l = 0, n = 1, 2, \dots$. Although we considered polar modes, this formula is also valid for non-polar ones, e.g., in Si nano-crystals. The SO modes can be included in the same manner, since the displacement field for them is also known [9] and the corresponding oscillator strengths can be calculated, but obviously the overlap integral (6) is several times less for these modes. We have discussed another mechanism of scattering, relevant for ensembles of nano-crystals of polar materials, by a collective longitudinal excitation spanning coherently many spheres. Combining the collective and confined LO scattering cross-sections we were able to describe the lineshapes in Raman spectra of the SiO₂ films doped by CdS nano-crystals.

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